Tanning Studies with Epoxy Resins*

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Although the chemical properties of 1,2 epoxides have been well established for some time, it is only recently that the interaction of this class of organic compounds with proteins has been reported. In 1944 Fraenkel-Conrat[1] reported the reaction of ethylene oxide, propylene oxide, and epichlorohydrin with various water soluble proteins. Interaction was readily accomplished under mild conditions and in aqueous solution. The isoelectric point of the treated proteins was increased by 1 to 3 pH units, indicating that the carboxyl groups were largely esterfied. Amino, phenolic, and sulfhydryl groups also appeared to participate in this reaction.

Fearnley and Speakman[2] investigated the action of diepoxybutane on wool and found that supercontraction of wool was prevented, presumably because of formation of new cross linkages between carboxyl groups of peptide chains. In contrast Alexander el al.[3] observed that only epichlorohydrin esterified the carboxyl groups of wool to any considerable extent.

Sykes[4] investigated the reaction of propylene oxide, epichlorohydrin, and vinyl cyclohexene dioxide with sheepskin collagen. The monofunctional propylene oxide had little effect on the structural stability of collagen. In alkaline solution epichlorohydrin caused an increase in shrinkage temperature (Ts) to about 78° C. (after three to seven days) comparable to aldehyde tannage. The diepoxy compound, vinyl cyclohexene dioxide, tanned collagen over a wide range of pH. Although the shrinkage temperature (72°C) was not very high the bonds introduced were stated to be exceptionally stable.

Immendorfer[5] studied the tanning action of various other epoxides. It was reported that firm, full, supple and well tanned leathers were obtained upon treatment of hide or calfskin with 15-20% by weight of butadiene monoxide, butadiene dioxide, butanediol diglycidyl ether, phenoxybutene oxide and epichlorohydrin.

Within recent years the epoxy resins, a new class of condensation polymers, have become commercially available. In general these are condensation products of epichlorohydrin with bisphenol[6-11]. The commercial resins are mixtures of polymers with molecular weights in the range of about 400 to 8000[7]. An important structural feature of these epoxy resins is the presence of terminal glycidyl ether groups, so that they can be considered as diepoxides. Hence it was of interest to investigate the behavior of the epoxy resins toward

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hide substance. Exploratory work indicated that one of the epoxy resins was particularly suitable for treatment of hides in aqueous system. This paper is a preliminary report on tanning with this resin in aqeous suspension.

Experimental

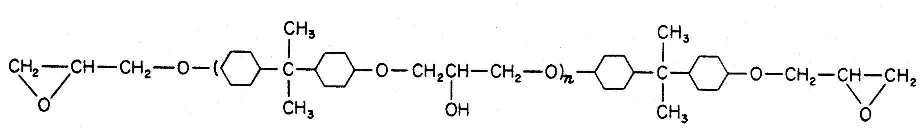
Materials. Limed cowhides and pickled calfskins were obtained from local tanneries. The cowhides were thoroughly rinsed and then pickled in a hydrochloric acid—sodium chloride pickle. The pickled raw materials were stored in a cold room at 36° F. Before tanning, the hides and skins were depickled by treating for 5 to 6 hours with sodium bicarbonate solution (pH 6.5), washed in water for 24 hours, treated for 7 to 8 hours with sodium acetate—acetic acid buffer (pH 4.9), washed in water for 24 hours, then dehydrated with acetone.

The epoxy resin used in this study was Epon 562.***

Treatment with Epoxy Resin. Small strips, approximately 1 x 3 inches, were cut from the acetone dehydrated cowhide or calfskin. About 10 g. of the cowhide and 6.5 - 8.0 g. of calfskin were used in the various treatments with the epoxy resin. These samples were wet back with water and generally 100 ml. of water or 0.2M buffer solution, 10 g. of various salts, and 5 g. of Epon 562 were added. The reaction was carried out at room temperature in closed bottles which were gently agitated by rolling on a low speed jar mill. Specimens, ¼ x 2-⅛ inches were periodically removed, rinsed thoroughly, and the shrinkage temperature (Ts) determined. The Ts was determined on freely suspended specimens mounted in a holder accommodating four samples. A few spot checks indicated that the Ts agreed reasonably well with the values obtained using the Theis shrinkage meter. After shrinkage the specimens were immersed in cold water to observe reversibility of shrinkage. After six days of treatment the remaining sample was thoroughly washed in water, allowed to air dry, and examined for leather-like appearance. The data are summarized in Tables I and II.

Discussion

The epoxy resins, which have recently become available, are in general condensation products of epichlorohydrin and bisphenol -A and the following structure has been postulated [6—11].



***Obtained from Shell Chemical Corp., 500 Fifth Ave., New York 36, N. Y. The mention of specific brands or companies is not to be construed as an endorsement by the United States Department of Agriculture of these brands or companies over those not mentioned.

TABLE I

Tanning Cowhide with Epon 562[a]

Exp. No.	Buffer	Salt	pH[b]	Shrinkage Temperature, °C.[c]				
				8 hours	1 day	2 days	3 days	6 days
1	Lactic acid, 0.2M	None	2.5–2.6	59	55	59	61	57
2	" "	NaCl	4.2–8.7	58	64	65	69	67
3	" "	Na_2SO_4	3.7–4.2	55	61	60	62	66
4	" "	$MgSO_4.7H_2O$	3.2–3.5	55	56	58	63	58
5	Sodium lactate, 0.2M	None	6.4–7.8	65	71	75[d]	77[d]	77[d]
6	" "	NaCl	10.0–9.6	72	78	80[e]	81	80[e]
7	" "	Na_2SO_4	8.6–9.1	68	77	78	82[e]	82[e]
8	" "	$MgSO_4.7H_2O$	7.8–8.6	66	68	74[d]	78[d]	77[e]
9	Water	None	5.8–7.3	66	69	77[d]	80[d]	79[d]
10	"	NaCl	10.0–9.8	69	76	77	81	79[e]
11	"	Na_2SO_4	8.6–9.6	67	74	77[d]	81[e]	82[e]
12	"	$MgSO_4.7H_2O$	8.1–8.8	63	67	70	76[d]	76[e]
13	$NaHCO_3$, 0.2M	None	8.1–8.3	68	74	75[d]	77[d]	76[d]
14	"	NaCl	9.0–9.2	70	74	79[d]	79[d]	77
15	"	Na_2SO_4	8.2–8.7	70	77	78[d]	81[e]	80[d]
16	"	$MgSO_4.7H_2O$	7.6–7.8	69	72	73	75	75[d]
17	Na_2CO_3, 0.2M	Na_2SO_4	10.0–9.8	74	80[d]	78[d]	80[d]	83[e]
18	$Ca(OH)_2$, saturated	None	9.1–9.0	78[e]	80[d]	80[d]	81	80[d]
19	"	Na_2SO_4(2.5g)	11.2–10.8	73	75	—	78[d]	78[d,f]
20	"	Na_2SO_4(5 g)	10.7–11.0	75	76	—	82[e]	82[e,f]
21	"	Na_2SO_4	10.8–11.1	79[d]	78[d]	—	86[e]	86[e,f]
22	"	NaCl	10.3	77[d]	79[d]	77[d]	79[d]	79[e]
23	"	$MgSO_4.7H_2O$	9.1–9.2	64	68	84[e]	77[d]	77
24	$Ca(OH)_2$, 1.0 g.	Na_2SO_4	12.0–11.8	68	71	85[e]	85[e]	84[e]
25	MgO, 1.0 g.	None	10.2–9.9	64	70	—	79	82[d,f]
26	"	Na_2SO_4	10.4–10.2	66	75	—	81[e]	83[e]

a. Hide (Ts=60°C) generally equilibrated overnight with buffer or buffer salt solution before adding Epon 562. Ten grams of salt were present in the aq. solution unless otherwise noted.
b. Range for the 8 hour to 6 day interval.
c. Samples washed for about 1 day in tap water.
d. Ts specimens showed good recovery of length (Ca 90–96%) on cooling.
e. Ts specimens showed excellent recovery of length (96–100%) on cooling.
f. Treatment carried out for 5 days.

Epon 562, one of the epoxy resins, is stated to be an aliphatic modification[6]; a condensate of glycerol (rather than bisphenol) with epichlorohydrin[12]. In both types of resin the terminal groups of the chain are probably glycidyl ether groups and hence may be considered examples of commercially available diepoxides. Epon 562 is a moderately viscous liquid (viscosity C to F on the Gardner-Holdt Scale) having an equivalent weight (as an epoxide) of 140–165. It apparently is of low average molecular weight probably about 300, and slightly soluble in water.

It was found that Epon 562 reacted under mild conditions and in aqeous suspension to effect a tanning action on cowhide and calfskin. The tanning action was accompanied by an elevation of the shrinkage temperature and

TABLE II

Tanning Calfskin with Epon 562[a]

Exp. No.	Buffer	Salt	pH[b]	Shrinkage Temperature ° C.[c]				
				8 hours	1 day	2 days	3 days	6 days
1	Lactic acid, 0.2M	None	2.4	58	60	59	55	59
2	" "	Na_2SO_4	3.1–3.7	52	57	57	64	61
3	Sodium lactate, 0.2M	None	6.6–7.9	64	68	73	74	77[e]
4	" "	NaCl	10.0	68	79	80	81[d]	80[d]
5	" "	Na_2SO_4	7.8–9.6	64	71	78	82[d]	82[d]
6	Water	None	5.7–7.0	65	65	73	74	78[e]
7	"	NaCl	10.0	66	76	78	78	78
8	"	Na_2SO_4	7.9–10.7	64	70	76	81	83[e]
9	$NaHCO_3$, 0.2M	None	8.6–8.5	68	70	73	74	74[d]
10	"	NaCl	8.7–9.1	66	69	73	75	76
11	"	Na_2SO_4	7.9–8.6	66	73	75	79	81[d]
12	Na_2CO_3, 0.2M	None	10.5	72	77	75	79	77[d]
13	"	NaCl	10.2–10.0	79[e]	82[e]	83[d]	83[e]	82[d]
14	"	Na_2SO_4	10.2	81[d]	85[e]	85[d]	87[e]	86[e]
15	$Ca(OH)_2$, saturated	None	9.9–9.8	77	79	79[d]	75	80
16	"	Na_2SO_4 (2.5 g)	10.0–11.1	73	75	—	79	79[f]
17	"	Na_2SO_4 (5 g)	10.1–11.3	78	80	—	82[d]	82[d,f]
18	"	Na_2SO_4	10.2–11.3	85[d,g]	87[e]	—	88[e]	89[e,f]
19	"	NaCl	10.6–10.8	77[d]	78[d]	80[d]	82[e]	80[d]
20	MgO, 1 g	None	10.0–9.9	70	78	—	82[d]	82[e,f]
21	"	Na_2SO_4	10.1–10.3	78[d]	85[e]	—	85[e]	85[e,f]

a. Calfskin (Ts=60°C) generally equilibrated overnight with buffer or buffer salt solutions before adding Epon 562. Ten grams of salt were present in the aqueous solution unless otherwise noted.
b. Range for the 8 hour to 6 day interval.
c. Samples washed for about 1 day in tap water.
d. Ts specimens showed good recovery of length (Ca 90–96%) on cooling.
e. Ts specimens showed excellent recovery of length (96–100%) on cooling.
f. Treatment carried out for 5 days.
g. Ts after 4 hours was 82° C. with excellent recovery of length on cooling.

reversible shrinkage. These two properties were of value in following the course of the reaction. Little if any tanning effect or reaction appeared to occur at pH below about 6. In the more alkaline range, pH above about 9, however, reaction appeared to be effected in a relatively short time. Tanning, as judged by the shrinkage temperature and reversibility of shrinkage, was effected in a period of from 8 hours to 6 days depending on the conditions. Sodium carbonate, magnesium oxide, or lime water, used with sodium sulfate, appeared to be the most desirable medium for effecting reaction or tanning, at least as regards the rate at which maximum Ts and reversible shrinkage are attained. In general the shrinkage temperature was elevated to approximately 80–85° C. Usually good reversibility of shrinkage was not observed until the Ts reached about 80° C. A sample of the leather prepared as in Experiment 21, Table I (6 days of treatment) was submitted to five successive shrinkages in a Theis meter. The specimen regained its original length on cooling each time. The Ts values were 83, 80, 79, 79, and 78° C., successively. A sample of formaldehyde tanned material, which also is known to shrink reversibly, showed the following successive Ts values: 89, 75, 69, 67, and 61° C. It is apparent that tanning with Epon 562 results in bonds, probably cross-linked, having a high degree of stability. The leather, after repeated shrinkage, was still flexible and leather-like when dried. When a wet back piece of Epon 562 tanned cattlehide (approximately two inches square) was immersed in boiling water for one minute it shrunk to about 75% of its original area, and regained its original area when placed in cold water.

Particularly in the alkaline pH range, using sodium carbonate, lime water, and magnesium oxide to control pH, the use of inorganic salts such as sodium sulfate resulted in more rapid reaction and a product with better leather characteristics. Sodium sulfate was considerably more effective than sodium chloride or magnesium sulfate probably because the former salt functions as a more active swelling depressant in alkaline solutions[13]. An aqeous sodium sulfate solution which was about 10% by weight with respect to the salt appeared to give the best results. Sodium chloride is probably not a suitable salt to use in this treatment because of the known tendency of epoxides to add hydrogen chloride even from neutral solutions[14]. When sodium carbonate, magnesium oxide, or lime water were used to regulate the pH, along with sodium sulfate, tanning with Epon 562 resulted in suitable leather products from cowhide in one to three days and from calfskin in less than one day.

Summary

Epon 562, an epoxy resin which is commercially available, was found to interact with cowhide and calfskin in aqeous systems to produce a tanning effect. Little if any reaction or tanning appeared to take place in the pH range below about six. High pH seemed most suitable for this reaction as regards the rate at which maximum Ts and reversibility of shrinkage are attained. Treatment with Epon 562 in sodium carbonate, magnesium oxide, or lime water in the presence of sodium sulfate gave the best results. Suitable leather products were obtained from cowhide in one to three days (Ts 80–85° C.) and from calfskin in less than one day (Ts about 85° C.). The leather exhibited the unusual property of reversible shrinkage with no visible damage to leather appearance after shrinkage.

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Discussion

Dr. Wallace Windus (Tanimex Corporation): Dr. Filachione and his associates have done an interesting piece of work. It is striking how the conditions resemble the classical method of tanning with formaldehyde—both being on the alkaline side to best advantage, and also the reversible shrinkage is similar.

This suggests that possibly the mechanism of the two tannages are closely related, if not the same. I think it is gratifying that possibly in this case we will have a reversal of the usual procedure of defining the mechanism of tanning before a complete evaluation from a practical standpoint. Perhaps the scientist is finally catching up with the art.

I have only one comment in connection with physical properties being somewhat poorer in some instances. As we all know this depends to some extent, perhaps a large extent, on the amount of tanning material that is used.

Conventional tanning materials if used in excess, produce over-tanning and lower the physical data. In this case approximately 20 to 25 per cent of the epon resin was used on a wet basis. This may be more than is necessary, providing the shrink test will be satisfactory with a smaller amount of material. If less can be used, I think the physical data will be improved. I think there are perhaps a number of questions. Mr. Lotz will now comment.

Mr. W. Robert Lotz (Albert Trostel and Sons): I think the very fact that our author has defined his paper as being in the nature of a progress report sets the pace for the discussion which must follow. Have we questions from the floor?

Dr. Ludwig Seligsberger (Quartermaster Research & Development Center): I just wonder whether you have determined the pH of the leather after washing because I think, maybe you have a little too high a pH.

DR. FILACHIONE: It takes a long time to wash alkali out of the samples. We usually wash these for a period of twenty-four hours; but before running the titration curve the ground-up specimens were electro-dialyzed, so we feel that this particular sample was free of all the inorganic ions that might be absorbed.

MR. FRANK CHADWICK (Atlas Refinery): There has been comment that the epoxy resins are highly toxic. Can you discuss this point from a production level?

FILACHIONE: I am afraid I cannot. I have not asked the suppliers of the resins for any specific information on toxicity. The label on Epon 562 carried the following caution: "this material should not be taken internally. Avoid prolonged contact with skin".

DR. WILLIAM J. MCDERMOTT (Rohm & Haas): Regarding toxicity, aren't these materials oil soluble? Wouldn't they be absorbed into the skin and since they are highly reactive, would you not expect them to react with the protein in the blood and also probably with the skin, itself? So you might end up with a dermatitis of some type. I would suspect that because of their reactivity with proteins that they would be toxic, especially if they are oil soluble.

FILACHIONE: They are soluble in organic solvents.

MCDERMOTT: They do have oil solubility?

FILACHIONE: Probably not in hydrocarbon oils.

MCDERMOTT: I was thinking in terms of solubility in animal oils.

FILACHIONE: Preferred solvents are ketones, esters, and ether alcohols. They may have some solubility in vegetable or animal oils.

MCDERMOTT: My thought was that solubility in animal oils would permit absorption by the skin and reactivity with body proteins could result in a toxic effect. One other question: how about the light stability of the Epoxy resin-tanned leather?

FILACHIONE: I would think the stability would be exceptionally good. I think there are co-valent bonds introduced into the protein by treatment with the epoxides.

MCDERMOTT: Such tanning materials would have added interest, if they gave light-fast leather, providing it is possible to improve them sufficiently so as to give stronger leather.

FILACHIONE: Yes I believe there is this possibility.

MCDERMOTT: It has been mentioned that the physical weakness of Epoxy Resin-tanned leather might be due to the incomplete removal of alkaline materials. In the process of deliming you treat the raw stock with ammonium chloride, or similar salt as a part of the bating procedure. Could not such salts be used in the deliming or de-alkalizing of such leather to decide whether the weakness is due to incomplete alkali-removal or is inherent in the tannage.

FILACHIONE: You mean, use a deliming operation before testing?

MCDERMOTT: Yes, to make sure you have removed all of the alkaline material.

FILACHIONE: That may be what gives us these results. We would like to repeat some of these experiments and we will look into it.

MCDERMOTT: You use a straight wash?

FILACHIONE: We just wash with water for a day or so.

LOTZ: The question of the solubility in solvents brings to mind the use of the solvent system itself. Would you care to discuss what you think of the use of these epon resins in solvent systems?

FILACHIONE: We have done a little on solvent systems, but we thought it would be more desirable to use a water system. The reaction does not occur as rapidly in the presence of solvent. We have used this resin as well as some of the other epoxy resins in fifty per cent acetone water systems and the shrink temperature did not get as high and the reaction seemed slower.

I think we let the reaction go on for about twelve days in the solvent system, whereas here we considered that we were finished before six days.

DR. STUBBINGS (Lehigh University): Have you tried the epoxy resin as a retannage of a chromium tanned material?

FILACHIONE: We have tanned these epoxy tanned materials with both vegetable and chrome in a qualitative way. They do take up a chromium or vegetable tanning material.

STUBBINGS: Have you tried the reverse—tanning with the epoxy material on top of a chromed tanned leather?

FILACHIONE: We did, but it did not seem to be very suitable because we preferred to treat with this resin in an alkaline medium and we did not get anything that looked too good.

MR. ANDREW J. GARD (The Dow Chemical Company): Did you run the determination on chrome?

FILACHIONE: We did not. We did run shrink temperature of the vegetable retanned material.

GARD: Was there a change that might indicate a stripping of the resin?

FILACHIONE: No, there was an increase in the shrink temperature when we retreated with vegetable—about five to ten degrees.

MR. FRANK EDMONDS (American Cyanamid Company): On the question of retanning with the vegetable, did you drop the pH of that leather with acid so that you could vegetable tan?

FILACHIONE: I think we generally used pH's of around 5—the natural pH of the extract, which was sulphited quebracho and chestnut. It was 5, or a little below that.

MR. W. O. DAWSON (Chemtan Company): I would like to state this: these products are notoriously water-in-soluble. Also Epon 562, being the lowest molecular weight product of the group, is the most water-soluble of this group of compounds sold by Shell. Did you determine the efficiency of the Epon 562? Secondly, have you investigated or inquired from Shell whether or not there may be methods of solubilizing the Epon 562 so that it can be used in a water system without resorting to the use of an emulsifying agent or suspending agent which system you used in your experiments?

FILACHIONE: To answer the first part, we generally just standardized on using a weight of Epon 562 which was 50 per cent of the acetone dehydrated hide material. And we did not try to determine the lowest quantity of Epon 562, which we could use to treat the protein. But I am sure it is considerably below the fifty per cent figure that we used.

Often in our runs we would see the insoluble layer of presumably unreacted Epon 562 at the end of the six-day period. And we generally tested the solution qualitatively for epoxide and there was always epoxide present at the end of the six days.

There may be some side reaction and I think the most important one probably would be hydrolysis of the epoxide by the water. But that should be fairly slow.

In all of these other treatments of proteins with epoxide they generally carry out the reaction for six or seven days and apparently the rate of hydrolysis is slow. In actual commerce, when they want to hydrolyze epoxides they generally use acid catalysts for increasing the rate of hydrolysis of the oxide ring.

There was another part to your question: we have not asked Shell or have not tried to obtain any information on whether these resins can be solubilized. We used the straight suspension in water and the emulsifying agent in water, and you would expect the emulsifying agent to increase the solubility, but it appeared to behave similarly to the unemulsified system, so that we assumed that, if it did increase the solubility, it did not increase it enough to alter the rate of the reaction.

MR. LOTZ: If there are no more questions it is papers like this that represent the building blocks for making new tannages. As a practical leather man I appreciate that this is only the beginning. It is in the nature of a progress report. At the same time, work done here can be expanded into things which can be turned into dollars and cents by the tanneries.

I want to thank Mr. Filachione for his paper and for the presentation. I am sure if you have further questions he will be glad to answer them after the morning session.